

Self-interaction correction in a simple model

P. M. Dinh^{a*}, J. Messud^a, P.-G. Reinhard^b, and E. Suraud^a

^a*Laboratoire de Physique Théorique, Université Paul Sabatier, CNRS
118 route de Narbonne F-31062 Toulouse Cédex, France*

^b*Institut für Theoretische Physik, Universität Erlangen,
Staudtstrasse 7 D-91058 Erlangen, Germany*

Abstract

We discuss various ways to handle self-interaction corrections (SIC) to Density Functional Theory (DFT) calculations. To that end, we use a simple model of few particles in a finite number of states together with a simple zero-range interaction for which full Hartree-Fock can easily be computed as a benchmark. The model allows to shed some light on the balance between orthonormality of the involved states and energy variance.

Key words: Density Functional Theory, Self-Interaction Correction, Orthonormality of wavefunctions
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1 Introduction

Density Functional Theory (DFT) [1,2,3,4,5,6,7] is a standard theoretical tool for the description of electronic systems, which takes into account exchange and correlation effects. Practically, DFT methods require approximations to the exchange and correlation potentials. The most widely used is the Local Density Approximation (LDA) [5]. This scheme however contains a spurious self-interaction. As a consequence, the Coulomb asymptotics, the ionization potential, and the potential energy surface of a system turn out to be wrong. These incorrect behaviors can lead to misleading results especially in time-dependent processes, as e.g. dynamics of ionization.

* Corresponding author

Email-address : dinh@irsamc.ups-tlse.fr

A corrected description includes a self-interaction correction (SIC) [8,9]. SIC methods were tried and tested in various domains of physics, such as atomic, molecular, cluster and solid state physics, see e.g. [10,11,12,13,14,15,16,17,18]. The original SIC scheme leads to an orbital dependent (and thus non hermitian) mean-field which, as a consequence, leads to violation of orthonormality. That problem has been attacked with various strategies. When maintaining orbital-dependent potentials, the most consistent technique is to deal with a matrix of Lagrangian multipliers taking care explicitly for orthonormality, see e.g. [12]. A formally elegant alternative is to enforce a common mean-field potential by the method of optimized effective potentials (OEP) [19] which, however, can become technically very involved. Thus one often steps down to the Krieger-Li-Iafrate (KLI) approximation for OEP [20]. KLI-SIC is widely accepted as a useful and inexpensive approach to SIC. There are, however, some drawbacks showing up in critical applications. Indeed KLI is underestimating the often necessary localization of wavefunctions [21] which, e.g., leads to problems with the polarizability in chain molecules [22,23] or with NMR shieldings [24]. Time dependent KLI also runs in serious problems with energy conservation and zero-force theorem [25]. Thus there remains a need for a direct handling of SIC to deal with such critical applications. The non-hermiticity of the orbital-dependent mean-field and proper handling of orthonormality of the occupied single-particle states are then crucial topics to be considered, particularly in time-dependent applications. The formally sound, but practically cumbersome, way to deal with that is to use a full matrix of Lagrange multipliers. It is widely used practice to abbreviate that by using standard diagonalization schemes together with explicit orthonormalization. It is the aim of the present paper to compare various solution strategies and to investigate in detail the interplay of orthonormality and energy diagonality (or variance, respectively). This will be done in a simplest model involving two active states.

The paper is organized as follows : Section 2 introduces the model, section 3 summarizes briefly the various approaches, and section 4 is devoted to discussion of results.

2 The two-state model

2.1 The model Hamiltonian

We consider four electrons, two spin-up and two spin-down, in one spatial dimension with the Hamiltonian

$$\hat{H} = \hat{h}_0 + \hat{V} \quad , \quad \hat{V} = \frac{g}{2} \sum_{i \neq j} \delta(r_i - r_j) \quad , \quad (1a)$$

$$\hat{h}_0 = -\frac{\hat{\Delta}}{2} + U_{\text{ion}} \quad , \quad U_{\text{ion}} = -\frac{e^2 q}{\sqrt{(r - r_0)^2 + a^2}} - \frac{e^2 (Q - q)}{\sqrt{(r + r_0)^2 + a^2}} \quad . \quad (1b)$$

The electron-electron interaction \hat{V} is taken schematically as zero range. The external ionic potential is regularized at short distance. Its parameters are chosen as $r_0 = 4 a_0$, $a = \sqrt{5} a_0$, total charge $Q = 2$ and charge in the right well $q = 1.5$. The potential has two centers around $\pm r_0$ and the charge q creates a spatial asymmetry, see Fig. 1. The ratio e^2/r_0 sets the natural energy unit.

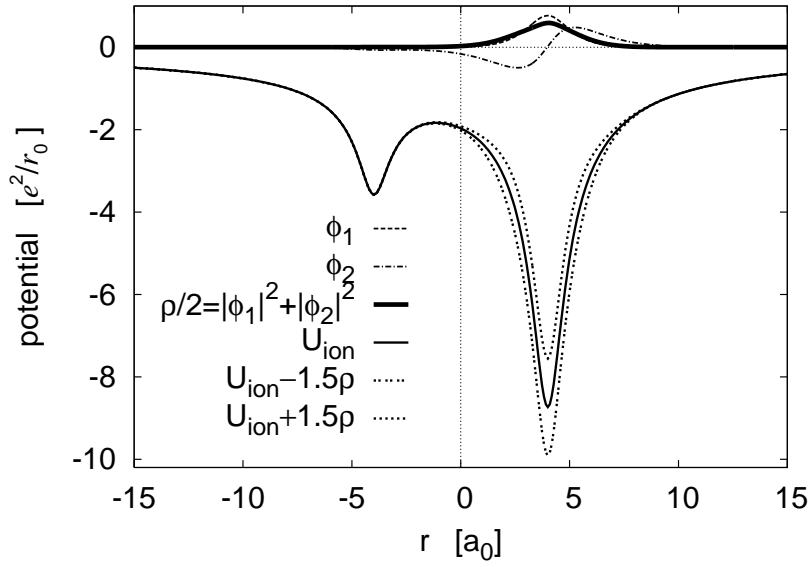


Fig. 1. Potential U_{ion} (full thin line), eigenfunctions ϕ_1 (long dashes) and ϕ_2 (dashes and dots), and half the density $\rho/2 = |\phi_1|^2 + |\phi_2|^2$ (full thick line), obtained from the unperturbed Hamiltonian \hat{h}_0 , plotted as a function of r . Two perturbed potentials are also presented, namely $U_{\text{ion}} - 1.5\rho$ (short dashes) and $U_{\text{ion}} + 1.5\rho$ (dots).

In order to make the comparison of the different SIC schemes more transparent, we study the interacting problem in a small basis of two states. These basis states are generated from solving first the unperturbed problem, $\hat{h}_0|\phi_{i\sigma}\rangle = \epsilon_i^{(0)}|\phi_{i\sigma}\rangle$, where $\sigma \in \{\uparrow, \downarrow\}$ is the spin label and i counts the level sequence which is generated for σ . Note that \hat{h}_0 is hermitian and thus the $|\phi_{i\sigma}\rangle$ are orthonormal. The case is fully symmetrical in both spins. Thus we will drop in the following the spin labels wherever this causes no ambiguities. We take for further considerations the energetically lowest two states, i.e., $i = 1, 2$. The ϕ as well as the total density in a given spin subspace, $\rho(r)/2 = |\phi_1(r)|^2 + |\phi_2(r)|^2$, are plotted in Fig. 1. One can also see in this figure the effect of an additional mean-field term $g\rho(r)$ for $g = -1.5$ and $g = 1.5$. A negative coupling constant corresponds to an extra attraction and the deepest well is deepened, while a positive coupling constant gives a repulsion and tends to decrease the

depth of the wells. The two-body interaction is taken into account at various levels of mean-field approximation. The corresponding mean-field solutions $\psi_{i\sigma}$ are expanded in the basis of the two occupied unperturbed states, i.e. $|\psi_{i\sigma}\rangle = c_{i1}|\phi_{1\sigma}\rangle + c_{i2}|\phi_{2\sigma}\rangle$ (a more suitable parameterization will be introduced later). This transformation redistributes components amongst occupied states and is thus concentrating discussions particularly on the SIC.

2.2 Energy expressions

The various methods used here can all be formulated in terms of the energy-density functional. The full HF case serves as a benchmark. The HF energy as derived from the full Hamiltonian \hat{H} (1a) reads

$$E^{(\text{HF})} = E_0 + \frac{g}{4} \int dr \rho(r)^2 \quad , \quad E_0 = 2 \sum_{i=1,2} \varepsilon_i \quad (2)$$

where the factor 2 in E_0 stands for spin degeneracy and $\rho(r) = 2|\psi_1(r)|^2 + 2|\psi_2(r)|^2$. Here the ψ denote the eigenfunctions of the perturbed \hat{H} . Note that the zero-range interaction \hat{V} produces a purely density-dependent energy already at the level of exact exchange. When only the Hartree contribution is taken into account, the energy is now given by

$$E^{(\text{Ha})} = E_0 + \frac{g}{2} \int dr \rho(r)^2 \quad . \quad (3)$$

This Hartree energy is deduced from the direct term of the interaction only. This raises the self-interaction problem. Augmenting that Hartree energy by a self-interaction correction (SIC) reads

$$E^{(\text{SIC})} = E_0 + \frac{g}{2} \int dr \rho(r)^2 - \sum_{i,\sigma} \frac{g}{2} \int dr \rho_{i\sigma}(r)^2 \quad , \quad \rho_{i\sigma}(r) = |\psi_{i\sigma}(r)|^2 \quad . \quad (4)$$

3 The mean-field equations in various approaches

The mean-field equations are derived from a given energy expression by variation with respect to the single-electron wavefunctions ψ_i . This reads in general

$$\hat{h}_i |\psi_i\rangle = \varepsilon_i |\psi_i\rangle \quad , \quad \hat{h}_i = \hat{h}_0 + U_i^{(\text{mf})} \quad (5)$$

where the self-consistent mean-field (mf) contribution $U_i^{(\text{mf})}$ from the electron-electron interaction depends on the actual level of approach. The unperturbed part \hat{h}_0 remains the same in all approaches. All further discussions concentrate on the mean-field potential. Note that the mean-field Hamiltonian may depend on the state i on which it acts. That will be a major topic in the following.

3.1 Hartree-Fock

In the Hartree-Fock (HF) scheme, the Fock term automatically cancels all self-interactions. It is the most complete approach in the variational space of Slater states and provides the reference theory as we work at the level of exchange only. The mean-field potential $U^{(\text{mf})}$ then reads

$$U^{(\text{HF})}[\rho] = \frac{g}{2}\rho(r) \quad . \quad (6)$$

It is hermitian and so becomes the total mean-field Hamiltonian $\hat{h}^{(\text{HF})} = \hat{h}_0 + U^{(\text{HF})}$. For then, the solutions of Eq. (5) are orthonormal. The mean-field equations can also be expressed in terms of matrix elements which reads, for the two-state model,

$$\langle \psi_1 | \hat{h}^{(\text{HF})} | \psi_2 \rangle = 0 \quad , \quad \varepsilon_i^{(\text{HF})} = \langle \psi_i | \hat{h}^{(\text{HF})} | \psi_i \rangle \quad . \quad (7)$$

3.2 Hartree

The situation is very similar to HF, except for a different factor in front of the mean-field potential. We have now, for $U^{(\text{mf})}$,

$$U^{(\text{Ha})}[\rho] = g\rho(r) \quad . \quad (8)$$

The further handling proceeds as for HF in the previous subsection. The off-diagonal elements have to fulfill $\langle \psi_1 | \hat{h}^{(\text{Ha})} | \psi_2 \rangle = 0$ and diagonal ones define the Hartree single-particle energies $\varepsilon_i^{(\text{Ha})}$. Note that the Hartree scheme is here considered as the analogue of the Local Density Approximation widely used in DFT.

3.3 SIC

Variation of the SIC energy (4) yields for the mean-field potential :

$$U_{i\sigma}^{\text{SIC}} = g\rho(r) - g|\psi_{i\sigma}(r)|^2 = U^{(\text{Ha})}[\rho] - U^{(\text{Ha})}[|\psi_{i\sigma}(r)|^2] \quad . \quad (9)$$

This mean-field potential now depends explicitly on the state on which it acts. Orthonormality of the solution of the mean-field equation (5) is not guaranteed anymore. Several strategies are used to deal with that complication. We will present three variants and compare them step by step.

3.3.1 Explicit orthonormalization *a posteriori*

A straightforward attack to the problem is to solve the eigenvalue equations (5) for each state separately and to apply explicit orthonormalization *a posteriori*, e.g. by a Gram-Schmidt procedure. This reads

$$\hat{h}_1|\psi_1\rangle = \varepsilon_1|\psi_1\rangle \implies \varepsilon_1, |\psi_1\rangle \quad , \quad (10a)$$

$$\hat{h}_i|\psi_i\rangle = \varepsilon_i|\psi_i\rangle \quad \& \quad |\psi_i\rangle \perp \{|\psi_1\rangle, \dots, |\psi_{i-1}\rangle\} \implies \varepsilon_i, |\psi_i\rangle \quad . \quad (10b)$$

The equations (10b) look seducing. However, one does not solve the eigenvalue problem for $|\psi_i\rangle$ in full but only in a restricted space where all states below have been projected out by the orthogonalization. We will denote that approach by the acronym “OSIC”. The price to be paid for that simplification will be checked in our detailed example below.

3.3.2 Orthonormality by Lagrange multipliers

A more satisfactory scheme consists in using Lagrange multipliers to impose the orthonormality constraint, $\langle\psi_j|\psi_j\rangle = \delta_{ij}$, at the level of the variational formulation following [26]. We will refer to this scheme by the acronym “LSIC”. The system one has to solve is then given by :

$$\hat{h}_i|\psi_i\rangle = \sum_{j=1,2} \lambda_{ij}|\psi_j\rangle, \quad i = 1, 2 \quad (11a)$$

where \hat{h}_i is defined in Eq. (5) and the Lagrange multipliers are given by $\lambda_{ij} = \langle\psi_j|\hat{h}_i|\psi_i\rangle$. Furthermore the orthonormality of the ψ imposes a “symmetry” condition on the λ_{ij} :

$$\lambda_{ij} = (\lambda_{ji})^* = \frac{1}{2}\langle\psi_i|\hat{h}_i + \hat{h}_j|\psi_j\rangle \quad . \quad (11b)$$

That equation is more involved than Eq. (5), since it is no longer an eigenvalue equation but they guarantee that the solutions ψ_i will be orthogonal. Furthermore, as Eq. (11b) stems from a variational principle on the energy in an effectively reduced space (orthonormal orbitals), it is necessary fulfilled.

The constrained equations (11) do not yield immediately single-particle energies as the λ_{ij} matrix is not diagonal. We thus define the $\varepsilon_i^{(\text{LSIC})}$ as eigenvalues of the constraint matrix λ_{ji} . Eq. (11b) shows that λ_{ji} is a hermitian matrix. Thus a diagonalization is possible and the definition makes sense.

3.4 Ignoring orthonormalization

One could be very naive and ignore the orthonormality at all. In our model, that amounts simply to solve the eigenvalue problem with $U_{1\sigma}$ associating the solution with lowest eigenvalue and with $U_{2\sigma}$ associating the highest eigenvalue. That naive SIC scheme will be labeled by the acronym N-OSIC for “non-orthonormalized SIC”, in order to stress the loss of orthonormalization of the eigenstates. We consider that, in principle prohibited, option for pedagogical purposes.

4 Comparison between HF, Hartree and SIC

4.1 Numerical handling in the two-state model

The aim is to check the simultaneous fulfillment of the mean-field equations (5) for each state $i = 1, 2$ in the two-state model together with orthonormality of the corresponding solutions ψ_i . We restrict the solutions to the configuration space spanned by the two energetically lowest eigenstates ϕ_1 and ϕ_2 of the unperturbed problem, see section 2.1. The solutions of the interacting mean-field equations will thus be expanded as

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \cos \theta_1 & -\sin \theta_1 \\ \sin \theta_2 & \cos \theta_2 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} \quad , \quad (12)$$

the same way for both spins. That transformation maintains normalization of the ψ . It becomes a unitary transformation if $\theta_2 = \theta_1$ and then also keeps orthogonality between the ψ . However we *a priori* start with $\theta_2 \neq \theta_1$.

Solution of mean-field equations means that the variance of the corresponding mean-field Hamiltonian becomes zero. Thus we consider as a global measure of convergence the squared deviations from the goal,

$$\chi^2 = \frac{\sigma^2}{\langle h \rangle^2} + \sin^2(\theta_2 - \theta_1) \quad , \quad \sigma^2 = \sum_i \Delta h_i^2 \quad (13)$$

where the mean field variances for HF, Hartree, N-OSIC and OSIC read

$$\Delta h_i^2 = \sum_j \left| \langle \phi_j | \hat{h}_i - \varepsilon_i | \psi_i \rangle \right|^2 \quad , \quad \varepsilon_i = \langle \psi_i | \hat{h}_i | \psi_i \rangle \quad , \quad (14a)$$

while in the case of LSIC, these expressions are more involved, due to the

Lagrange multipliers λ_{ik} ,

$$\Delta h_i^2 = \sum_j \left| \left\langle \phi_j \left| \hat{h}_i - \sum_k \lambda_{ik} \right| \psi_i \right\rangle \right|^2, \quad \lambda_{ik} = \frac{1}{2} \langle \psi_i | \hat{h}_i + \hat{h}_k | \psi_k \rangle. \quad (14b)$$

The mean value of \hat{h} is defined as $\langle h \rangle = \frac{1}{2} \sum_i \langle \psi_i | \hat{h}_i | \psi_i \rangle$. The solution is found by searching the global minimum of χ^2 in the space of the angles θ_1 and θ_2 . The natural result $\theta_1 = \theta_2$ emerges immediately for HF, Hartree and LSIC. The case remains open for N-OSIC and OSIC.

4.2 Result and discussion

Four coupling constants g have been tested : -1.5 , -0.5 , 0.5 and 1.5 . For all cases, the HF single particle energies correspond to bound states and the shifts in energy are rather small, consistently with the fact that our zero-range interaction potential is a perturbation of \hat{h}_0 , as we work in the basis of the eigenstates of \hat{h}_0 . For $g > 1.5$, the repulsion starts to be too strong and the eigenstates are less and less bound, or even not bound anymore.

In Fig. 2, we present the two eigen-energies ε_1 and ε_2 for the various schemes. Remind that the HF values represent our benchmark calculations. As expected, the Hartree calculation, which does not account for any SIC, gives values that are far from the HF energies. For negative coupling constants, the Hartree states are too bound, while for positive values, they are less bound. This is not a surprise, since comparing Eqs. (6) and (8), $U^{(\text{Ha})}$ is twice larger than $U^{(\text{HF})}$.

When SIC is included, the eigen-energies are very close to the HF results. Surprisingly SIC without imposing the orthogonality of the ψ (N-OSIC) works remarkably well, and actually the corresponding energies are indistinguishable from those of SIC with orthogonality.

However our concern is precisely the conservation of orthogonality. Following that aim, we have plotted in Fig. 3 two indicators of the resolution precision for each scheme : the ratio of the Hamiltonian variance over its mean value, $\sigma/\langle h \rangle$, see Eq. (13), for all SIC schemes, and the orthogonality violation of the ψ , $|\sin(\theta_2 - \theta_1)|$, only in the case of HF, Hartree, SIC, N-OSIC and OSIC. Note that such an indicator should not exist neither for OSIC nor for LSIC, since the orthogonality of the ψ is explicitly taken into account in both schemes. And indeed $|\sin(\theta_2 - \theta_1)|$ vanishes for LSIC as it should, for the orthonormalization of the ψ is imposed in the variational derivation of the total energy. However in OSIC, as is discussed in Sec. 3.3.1, the brute force orthogonalization restricts the space of the ψ and a vanishing minimum of the χ^2 , Eq. (13), may not exist. And this is indeed the case as we shall see below.

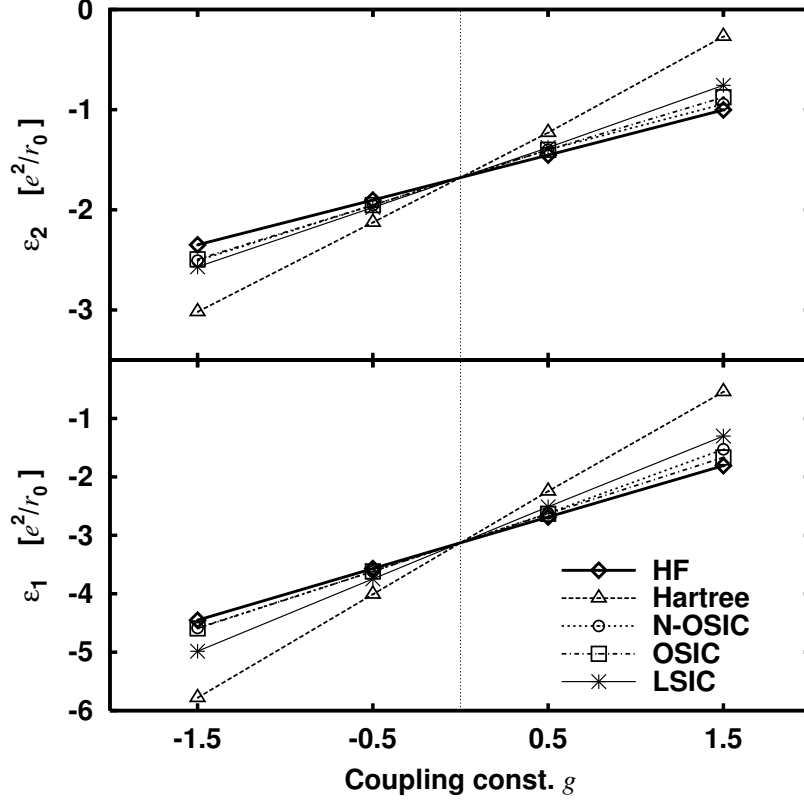


Fig. 2. Single particle energies of the eigenfunctions obtained from the perturbed Hamiltonian within different approaches : HF (circles), Hartree (triangles), SIC without orthogonalization (N-OSIC, circles), SIC with orthogonalization (OSIC, squares), and SIC with Lagrange multipliers (LSIC, crosses).

As expected, HF and Hartree, which are hermitian, give perfect indicators in the sense that they are equal to zero : $\sigma/\langle h \rangle$ is about 10^{-16} , while the orthogonality of the ψ is verified within an error less than 10^{-15} . In LSIC, we also obtain the same order of magnitude for $\sigma/\langle h \rangle$.

Now let us focus on the various SIC we have tested. In N-OSIC, Eqs. (10), the standard deviation of h is one order of magnitude higher than in LSIC but remains very small (less than 10^{-14}). However, since no orthogonality has been taken into account, $|\sin(\theta_2 - \theta_1)|$ does not vanish, as expected : it ranges from 3 % up to 25 %. When one minimizes at the same time the standard deviation of h and the orthogonality condition (OSIC scheme), one of course obtains a better indicator for the orthogonality of the ψ , as is visible in Fig. 3 when comparing circles (N-OSIC) with squares (OSIC). In the latter case, the orthogonality is violated by 0.4–5 %. But note that $\sigma/\langle h \rangle$ does not vanish as well : For small couplings, it varies between 1 % and 2 %, while it goes up to 11.5% in the worst case. This means that, in this example, it is impossible to solve in a satisfactory way Schrödinger equations with orthogonal eigenstates. And actually, the violation is shared among the orthogonality and the variance

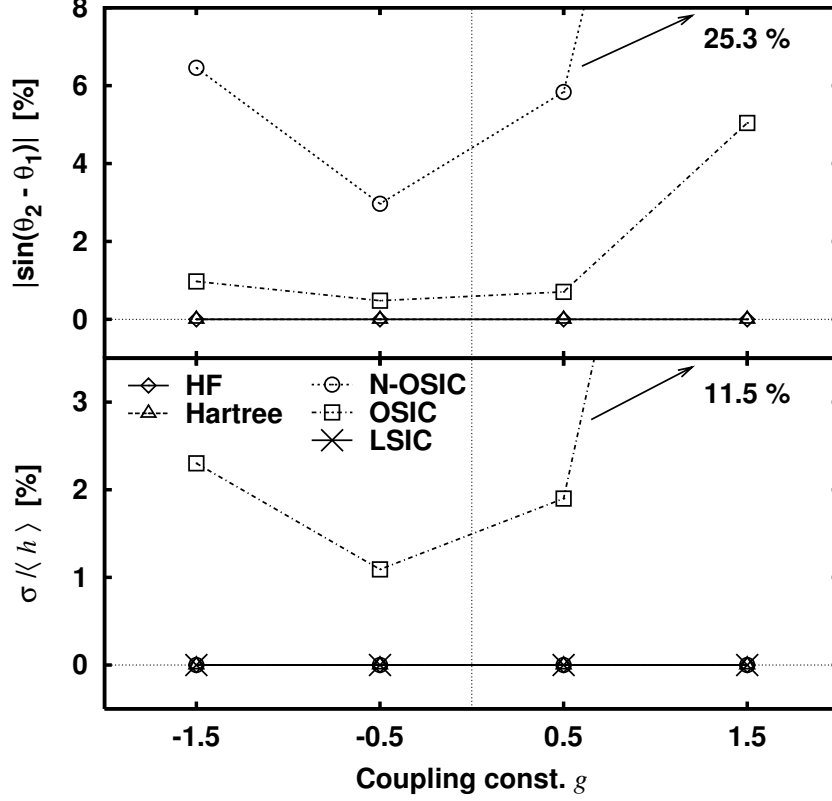


Fig. 3. Ratio of standard deviation over mean value of the Hamiltonian, $\sigma/\langle h \rangle$, and violation of orthogonality of the ψ , $|\sin(\theta_2 - \theta_1)|$, as a function of the coupling constant g : HF (diamonds), Hartree (triangles), SIC without orthogonalization (N-OSIC, circles), SIC with imposed orthogonality (OSIC, squares), and SIC with Lagrange multipliers (LSIC, crosses). In the upper panel, the orthogonality violation has no meaning for LSIC. In both panels, values for $g = 1.5$ are out of range, as indicated.

of h .

To end this section, we come back to the OSIC scheme. As stated just above, the violation of the vanishing of both orthogonality and variance of h is shared among these two constraints. One can actually give more weight to one condition with respect to the other one, for instance to the Schrödinger equations. In Fig. 4, we have plotted the results of the minimization of

$$f(\omega) = (1 - \omega) \frac{\sigma^2}{\langle h \rangle^2} + \omega \sin^2(\theta_2 - \theta_1) \quad , \quad (15)$$

where ω is a weight varying between 0 and 1, for a coupling constant of 0.5. We note that indeed, whatever the weight, both constraints are violated by the same order of magnitude. This means once again that it is impossible to meet both conditions at the same time in the OSIC scheme.

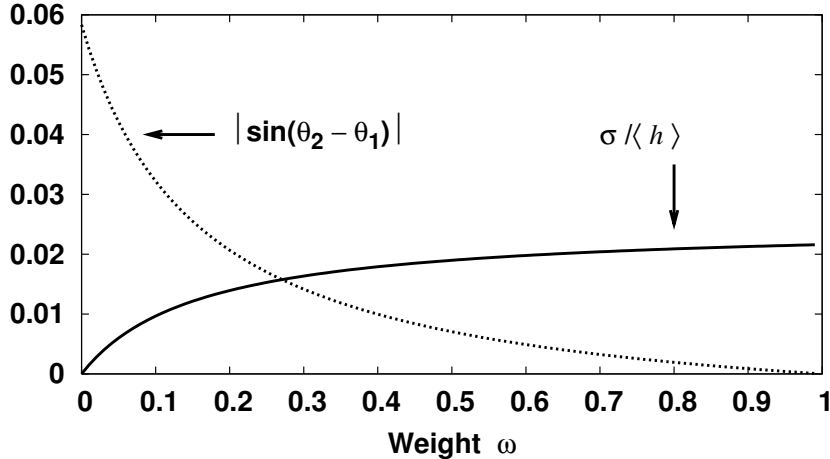


Fig. 4. Ratio of standard deviation over mean value of the Hamiltonian, $\sigma/\langle h \rangle$, (full line) and orthogonality of the ψ , $|\sin(\theta_2 - \theta_1)|$, (dotted line) as a function of the relative weight ω in the minimization of $f(\omega) = (1 - \omega)\sigma^2/\langle h \rangle^2 + \omega \sin^2(\theta_2 - \theta_1)$.

5 Conclusion

We have investigated the problem of orthonormality of the occupied single-particle states in mean-field equations with self-interaction correction (SIC). To that end, we have used a simple two-state model with zero-range interaction which concentrates fully on the share amongst the occupied states through SIC. The full Hartree-Fock (HF) case serves as a benchmark. The HF Hamiltonian is hermitian and we have energy diagonality together with orthonormality of the states. The same holds for the Hartree approach which, however, is plagued by the self-interaction error. SIC produces a state-dependent Hamiltonian and orthonormality becomes an issue. Naively ignoring that, yields deceptively good results for the energies but awfully wrong wavefunctions, with disastrous consequences for other observables. Taking care by explicit Gram-Schmidt orthonormalization during the mean-field solution provides acceptable results leaving, however, non-negligible variances in the energy. The error can remain small depending on the case. The consistent scheme dealing with a matrix of Lagrange multipliers is a bit involved and requires a separate step to defined single particle energy. But it is the only scheme delivering consistent and satisfying SIC results.

Note that, in static calculations, the orthonormalization may be a marginal problem in many cases as observables are found to stay very close to the HF ones. However it will build up to large errors in time-dependent cases and could even lead to divergencies.

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